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THE SOLVENT EFFECT IN THE HYDROGENATION OF CITRAL OVER Ir AND Ir-Fe/TiO_2 CATALYSTS

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ABSTRACT

The solvent effect in the citral hydrogenation over iridium catalysts has been studied. The catalysts used in this research were, the monometallic Ir/ TiO_2 reduced at low or high temperature (LT y HT) and the bimetallic Ir-Fe/TiO_2 (LT y HT) catalysts. As solvent n-heptane, an equimolar mixture n-heptane-1-propanol and 1-propanol were used. The reactions were carried out at a hydrogen pressure of 8.27 bar and at 363 K. In the LT catalyst, the catalytic activity increases upon the addition of Fe^{3+}. This positive effect was obtained keeping constant the selectivity to the unsaturated alcohol, being 100% selective to the products obtained by hydrogenation of the C=O bond. In the HT catalysts, both the addition of Fe and the presence of TiO_x moieties generated by the strong metal support interaction (SMSI) effect, lead to an increase of surface acidity. In LT and HT catalysts, an increase in the polarity of the solvent increases the catalytic activity, however the reaction pathway is modified by the presence of acid sites which in polar solvents allow the formation of acetals, mainly in the HT catalysts.

1. INTRODUCTION

The selective reduction of ⟨, β unsaturated carbonyl compounds is one of the most important research areas in fine chemistry; an overview of the topic is provided in several studies[1-13]. Crotonaldehyde [14-15], methacrolein [9], and particularly, cinamaldehyde [17] are the most widely documented compounds in this respect, particularly in relation to the use of single and two metal catalysts supported on various materials such as alumina, polymer, graphite, titania, etc. The main problem lies in obtaining catalysts affording the selective reduction of C=O thermodynamically less favored compared to the C=C hydrogenation.

The hydrogenation of ⟨, β unsaturated carbonyl compounds on single metal catalysts leads to the reduction of the conjugate C=C bond with a high selectivity. Suitable heterogeneous catalysts for the chemoselective hydrogenation of ⟨, β

unsaturated aldehydes are mostly based on supported noble metals such as Pd and Ru [18] and Ni supported in Al_2O_3 at lower hydrogenation pressure (2.3 bar) [19]. However, single metal may leads to the reduction of C=O bonds with the use of reducible support such as TiO_2 or Nb_2O_5 [20], which are able to produce the SMSI effect. Thus, this kind of system has been successfully used to increase the selectivity to the hydrogenation of C=O bond of the crotonaldehyde when a high reduction temperature of Pt-TiO_2 has been used [21]. Similar results have been obtained in the hydrogenation of acrolein over Pt and Ir metal supported on Nb_2O_5. In citral hydrogenation over Ir/TiO_2 catalysts reduced at high temperature HT (773 K), high selectivity (close to 100%) to the unsaturated alcohol has been reported by our group[22]. On the other hand, the formation of unsaturated alcohols over bimetallic catalysts have been obtained using Ru-Sn catalysts supported on carbon [23], Ir-Fe and Ir-Ge supported in SiO_2 [22], and those generated by the addition of Sn to Rh, Pt or Ru catalysts[24]. The favorable effect of the metal ions in these compounds (halides) is related to their Lewis acid character, which activates the carbonyl group by inducing positive charge on the carbon atom[25].

The textural properties of the support, particle size, extent of the metal dispersion, and nature of the precursor used to prepare the catalyst have also an effect on the selectivity of the reduction of ⟨, β unsaturated carbonyl compounds [1,22, 26, 27].

Citral is a very fascinating small molecule for selective hydrogenation, since it has three different double bonds, an isolated, a conjugated and a carbonyl group. Generally citral hydrogenation has been found to be sensitive to the variation of different reaction parameters. Particularly, the solvent used has a strong influence on the product distribution. It has been reported that it is possible to hydrogenate selectively the carbonyl bond with use of appropriate solvent. Arai et al.[28] pointed out the influence of solvent and pressure (50 bar H_2 and 170 bar CO_2) in the hydrogenation of three different ⟨, β unsaturated aldehydes, using supercritical CO_2 and ethanol over a conventional Pt/Al_2O_3 catalyst without any promoters. They reported high catalytic activity and selectivity close to 90%. Under the conditions used, unsaturated alcohols and saturated aldehydes were the main products. Very small quantities of saturated alcohols were detected, and in some cases other products (not identified) should be formed. The explanation given for the enhancement in the selectivity to the unsaturated alcohol is that the dielectric constant increases with an increase in pressure; in other words, the solvent is more polar at higher pressure. This may affect the reactivity of the polar C=O bond but not the less polar C=C bond. The C=O bonds are activated and easier hydrogenated leading to the selective formation of the unsaturated alcohols. Additionally, the density functional theory (DFT) has been used [29] to calculate and to compare the reactivity of the atoms present in the reactant molecule for a range of solvents with variable dielectric constant in citral hydrogenation under mild conditions using supercritical CO_2. They found that it is possible to hydrogenate selectively the conjugated and isolated C=C double bond of citral to a fully saturated aldehydes dihydrocitronellal. It was attributed to the fact that carbon dioxide molecule does not possess a permanent dipole moment. It has a quadrupole moment, which allows a stronger interaction with dipolar solutes. This quadrupole moment enable CO_2 to acts as both a Lewis acid and Lewis base that is recognized as being important in the CO_2 based solvatation. Furthermore, the dielectric constant of supercritical CO_2 varies with the change in density resulted from the pressure variation as observed by Arai et al.[28].

Aramendia et al.[30] have studied the reduction of citral in gas-phase by hydrogen transfer over acid-basic catalysts ($AlPO_4/SiO_2$, MgO, MgO/B_2O_3 and ZrO_2). The former is predominantly acid whereas the MgO and MgO/B_2O_3 are essentially basic, containing only few acid sites and the ZrO_2, which is an amphoteric solid, containing a similar number of acid and basic sites. The TPD-MS profiles for

pyridine and dimethylpyiridine were used to characterize the acid sites of the solids. They used different alcohols as hydrogen donor (aliphatic or aromatic alcohols) and they found that the hydrogen-transfer reductions of citral by 1-phenylethanol as hydrogen donor on basic catalysts (MgO or MgO/B_2O_3) lead to the selectivity reduction of the carbonyl group, whereas, acid and amphoteric solids lead to the completely selective reduction of the double bonds. The behavior is explained in terms of the interaction of the citral molecule and the catalyst surface, whether citral is adsorbed on the surface of the acid-base catalyst via its C=O or its C=C group, which in turn depends on the nature and strength of the catalysts sites. Thus, strong sites favor the reduction of the C=O bond whereas weak sites promote the reduction of C=C bond conjugated with the previous one. The alcohol used as hydrogen donor play a crucial role since it influences both conversion and selectivity in the hydrogenation process. Secondary alcohols (both aliphatic and aromatic) are effective hydrogen donors in this context, while the aromatic group provide a somewhat higher selectivity towards the reduction of the C=O group.

The main aim of the present work is to study the effect of metallic and acid sites and the SMSI state on the catalytic behavior in the citral hydrogenation over Ir catalysts. The effect of the polarity of the solvent on the activity and selectivity to the different products was also investigated.

2. EXPERIMENTAL

Ir/TiO_2 catalysts were prepared by wet impregnation of TiO_2 (P-25 DEGUSSA, S_{BET} = 72 m^2/g. m^2/g) with au aqueous solution of H_2IrCl_6 p.a. (Aldrich) to give an Ir loading of 1wt. %. The samples impregnates were dried under vacuum at 373 K for 6 h, calcined in air at 673 K for 4 h, and reduced *in situ* at 473 or 773 (LT or HT, respectively) for 2h prior to the characterization or catalyst test. Additionally, bimetallic Ir-Fe catalysts were obtained by impregnation of an aliquot of reduced Ir/TiO_2 catalysts with an aqueous solution of $FeCl_3$ at pH = 3 in an appropriate amount an iron content of 1 wt.%. After the impregnation, the solids were dried at vacuum at 343 K.

The reaction was conduced in a Parr Instrument Model 4561 autoclave at a constant stirring rate (1000 rpm) batch. All reactions were performed using an hydrogen pressure of 8.27 bar, catalyst weight of 300 mg, 40 ml of a 0.10 M solution of citral in solvent (heptane, n-heptane:1-propanol or 1- propanol) and reaction temperature of 363 K. Prior the reaction, the reactor was loaded with the catalyst and reactants at atmospheric pressure during 30 min and flowed with He through the solution to assure the absence of oxygen. Prior the experiment, all catalysts were reduced *in situ* under hydrogen flow of 20 cm^3min^{-1} at atmospheric pressure and temperature of 363 K. In all reaction, internal diffusion limitations were also shown to be absent by applying the Weisz-Prater parameter, which gave a value maximum of 0.19 [31]**.** Blank experiment showed no catalytic activity due to the support under these conditions. An HP 4890 GC furnished with an HP 5 semi-capillary column of 15 m and 0.53 mm ID analyzed reaction products. The GC analysis was performed using a flame ionization detector, using He as carrier, and the column was kept at a constant temperature, 393 K. Under these analytical conditions, the retention time of the reported reactants and products were citral (E): 30.7; citral (Z): 35.4; nerol: 27.6; geraniol 32.2 and acetals: 41 min. The presence of acetals were confirmed by the use of mass spectroscopy - Gases chromatography (GC-MS)

Nitrogen physisorption at 77 K and hydrogen chemisorption at 298 K were carried out in a Micromeritic ASAP 2010 apparatus. TEM micrographs were obtained in a microscope JEOL Model JEM -1200 EXII System and XRD in a Rigaku apparatus.

Adsorption of NH_3 was studied by a pulse method in a Micromeritics TPD/TPR 2900 apparatus. The samples were heated up to 383K and maintained at this temperature for 1 h in He flow. Then, doses of NH_3 were sent to the samples up to complete saturation. Later on the samples were cooled down to room temperature, and once the base line was restored, the temperature was increases linearly at a heating rate of 10°/min up to 800 K. Photoelectron spectra (XPS) were recorded using an Escalab 200 R spectrometer provided with a hemispherical analyzer, and using non-monochromatic Mg K X-ray radiation ***Qm*** *=1253.6 eV).* The surface Ir/Ti, Fe/Ti, Fe/Ir and atomic ratios were estimated from the integrated intensities of Ir 4f Fe 2p and Ti $2p_{3/2}$ lines after background subtraction and corrected by the atomic sensitivity factors [32]**.** The spectra were fitted to a combination of Gaussian-Lorentzian lines of variable proportion. The bonding energy of the Si 2p peak at 103.4 eV was taken as an internal standard.

3. RESULTS AND DISCUSSION

Table 1 summarizes the hydrogen chemisorption results, the estimated metal particle size obtained by TEM and the NH_3 uptake. These results revealed that the iridium is highly dispersed. In fact, the H/Ir surface ratio of the Ir/TiO_2 LT catalysts was 0.25. The Fe-Ir/TiO_2 LT catalysts display a substantially lower H/Ir, due to partial coverage of Ir crystallites by oxidized species of iron. In the Fe-Ir/TiO_2 HT catalyst, a slight drop in the H/Ir ratio compared with the monometallic catalyst was observed. This is explained taking into account the low value of the H/Ir ratio exhibited by the Ir/TiO_2 HT catalyst, due to covering of the Ir particles by TiO moieties generated by the SMSI effect: Studies performed by transmission electron microcopy (TEM) indicate that particle size of Ir/TiO_2 LT and Ir/TiO_2 HT samples are similar (2.5-2.6 nm) and confirm that the iridium is highly dispersed in all the catalysts. The incorporation of Fe promoter to the reduced Ir catalyst did not modify significantly the metal particle size, showing metal particle size close to 2.7 nm. Surface acidity measurements were carried out from NH_3 uptake by a pulse method and the results are compiled in Table 1. Even though the values seems to be rather high, the trend is the expected one. Both serie exhibit the same trends. The Ir/TiO_2 catalysts show higher amount of acid sites than the support and the bimetallic Ir-Fe/TiO_2 display even higher values. The acid sites may be attributed to residual chloride because the catalysts were obtained from chlorine containing precursors H_2IrCl_6, $FeCl_3$ and also by TiO_x moieties generated by partial reduction of titania. The number of desorbed ammonia molecules given in table 1, may include not only the acid sites but also a contribution of NH_3 physisorbed on the support. After subtracting the adsorption by the support, significant quantities of adsorbed ammonia either on Ir or Ir-Fe catalyst remains, indicative of acid sites, which are present in higher extent in Fe-Ir/TiO catalysts. To have an estimation of the strength of the acid sites, TPD profiles of the chemisorbed NH_3 was also registered and they are shown in Figure 1. In spite of a quantitative evaluation of desorbed species was not performed because of a simple integration of the desorption peaks is rather risky considering that the ammonia decomposition can also take place during the DTP experiments, specially on Fe-Ir/TiO_2 catalysts. The profiles exhibit a wide peak centered close to 500 K attributed to the desorption of ammonia adsorbed on weak acid sites and it is likely that they also include NH_3 physically adsorbed on the support. The TPD profile over Ir/TiO_2 samples LT and HT, display a second peak place in the temperature range 660-700 K assigned to the desorption of ammonia from stronger acid sites, associated to the presence of chloride ions on catalysts surface. As expected, in the Ir-Fe catalysts, the intensity of the second peak increases significantly due to the presence of higher chlorine content, but it shift approximately 80 degrees to lower temperatures.

Table 1. H/Ir ratio, metal particle size, and surface acidity of TiO_2 and Ir/ TiO_2 catalysts.

Catalyst	H/Ir	d_{TEM}, nm	NH_3 adsorbed, molec/g x 10^{19}
TiO_2 LT	–	–	2.56
Ir-FeTiO LT	0.25	2.6	4.45
Ir-$FeTiO_2$ LT	0.05	2.7	8.31
TiO_2 HT	–	–	2.55
Ir/TiO_2 HT	0.16	2.5	4.60
Ir-$FeTiO_2$ HT	0.02	2.7	9.20

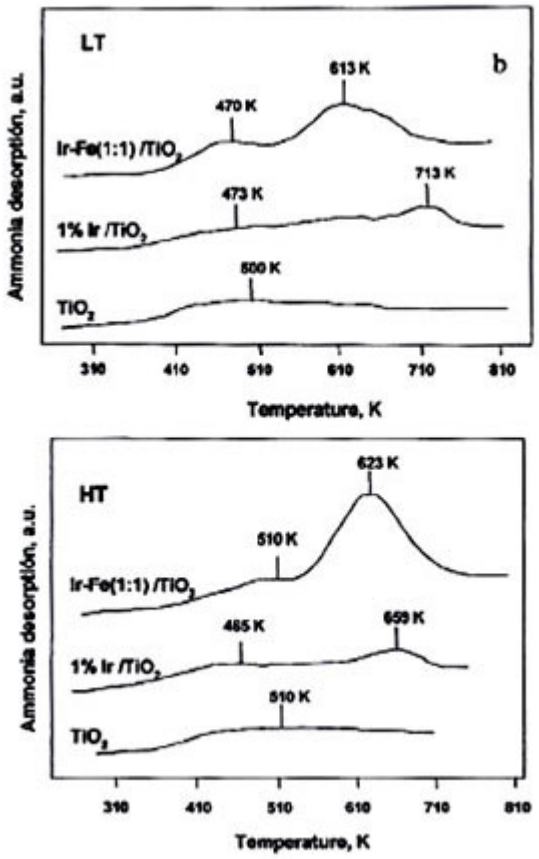

Figure 1. DTP of ammonia over Ir-suported catalysts. a) LT and b) HT series.

Binding energies of core-level electrons and metal surface composition were obtained from XP spectra.. For the Ir/TiO_2 LT catalyst, the binding energy of Ir $4f_{7/2}$ peak is approximately 60.4 eV, which corresponds to Ir^0 species. A slight increase in the BE of Ir $4f_{7/2}$ peak is consistent with the general trend observed for small particles of transition metal deposited on inorganic substrates, and agrees with

metal particle size obtained from TEM data. Catalysts promoted by Fe and titania-supported iridium catalysts reduced at high temperature display similar BE values. However, a slight broadening to higher binding energies suggests the presence of Ir0 and $Ir^{\delta+}$ species in these samples. Fig. 2 display XP spectra for some representative Ir-supported catalysts. It can be seen that three component had to be included to fit experimental spectra because the Ti 3s peak coming from the support falls just between the two spin-orbit split (Ir $f_{7/2}$and Ir 4f $_{5/2}$) levels of iridium.

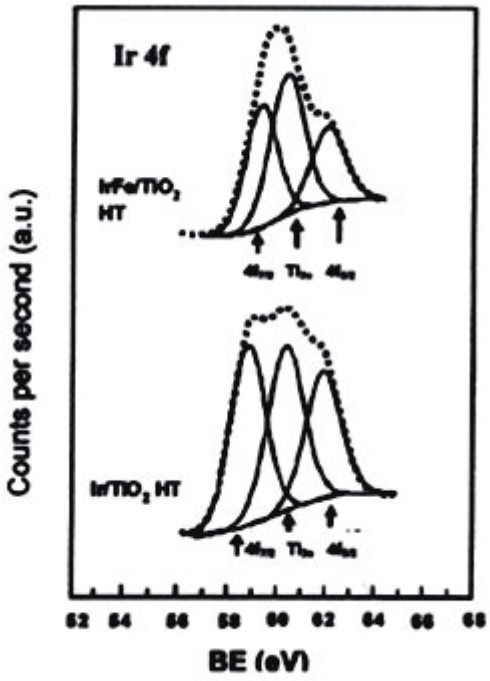

Figure 2. Ir 4f core-level spectra for Ir-suported catalysts.

hydrogenation, expressed as micromole converted per second per gram of catalyst and the initial turnover frequency, evaluated by means of the average of TOF at 10% conversion for the LT series. It should be pointed out that in the Ir/TiO_2 and Ir-Fe/ TiO_2- LT catalysts the selectivity towards the products obtained by hydrogenation of the C=O bond (geraniol and nerol) was 100 %. The proportion of nerol and geraniol is the same of the existing in the starting citral mixture 65:35, indicating that the hydrogenation of both isomers occurs at the same reaction rate.

Table 2 summarizes the observed $(Ir/Ti)_s$ and $(Fe/Ti)_s$ surface ratios for the studied catalysts. The Ir/TiO_2-HT catalysts show lower Ir/Ti ratios than their LT counterparts due presumably to the migration of TiO_x moieties on the Ir particles. For the Fe promoted titania-supported Ir catalysts, partial reduction of Fe_2O_3 additives in inferred as judging from the binding energies of Fe $2p_{3/2}$ levels.

Table 2. XPS atomic ratios of Ir-supported catalysts

Catalyst	$(Ir/Ti)_s$	$(Fe/Ti)_s$	$(Fe/Ir)_b$	(Fe/Ir)
Ir/TiO_2 LT	0.0242	---	---	---
Ir-Fe/TiO2 LT	0.0200	0.115	3.44	5.76
Ir/TiO_2 HT	0.0271	---	---	---
$Ir-Fe/TiO_2$ HT	0.0194	0.125	3.44	6.44

The (Ir/Ti) atomic surface ratio is comparable in both monometallic Ir/ TiO_2 catalysts and a slight decreases in that ratio takes place after the addition of Fe in both serie. This decreases account a surface coverage by iron species. On the other hand no significant changes in the (Fe/Ti) was observed in both bimetallic catalysts being these ratio 0.115 and 0.125, approximately 5 times higher than the bulk Fe/Ti ratio, confirming the surface enrichment in Fe. On the other hand, the surface $(Fe/Ir)]_s$ ratios of both $Ir-Fe/TiO_2$ (HT and LT) catalysts, were approximately two times higher than the bulk The slight increases in the mentioned ratio in the HT series suggest that the Fe species are covering not only the titania but also the Ir crystallites.

Catalytic hydrogenation results at 363 K and 8.27 bar, expressed as the evolution of the conversion level with time over Ir e Ir -Fe/TiO_2 LT catalysts on the studied solvents are displayed in Fig 3 a and b. It can be seen that all the catalysts showed similar trends. The reaction rates are higher at the beginning of reaction (below 2 h) and progressively decrease as the conversion increases. In both catalysts serie an increase in the polarity of the solvent leads to an enhancement in the conversion level. Tables 3 summarizes the conversion level at the same reaction time (1h) as well as the initial activity for citral hydrogenation, expressed as micromole converted per second per granm of catalyst and the initial turnover frequency, evaluated by means of the average of TOF at 10% conversion for the LT series. It should be ponted out that in the Ir/TiO_2 and Ir - Fe / TiO_2 LT catalyst the selectivity towards the products obtained by hydrogenation of the C = O bond (geraniol and nerol) was 100%. The proportion of nerol and geraniol is the same of the existing in the starting citral mixture 65:35 indicating that the hydrogenation of both isomers occurs at the same reaction rate.

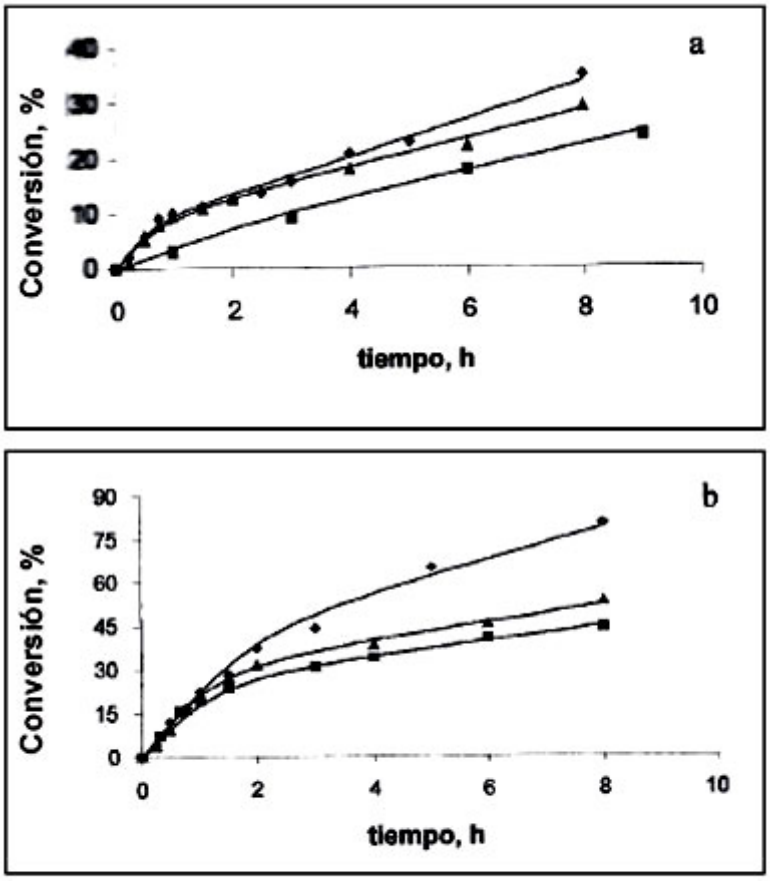

Figure 3. Evolution of the conversion level with time at 363 K and 8,27 bar in citral hydrogenation over Ir e Ir – Fe / TiO_2 LT catalysts and studied in three different solvents: (♦), 1- propanol; (▲), n-heptane y 1- propanol; (■), n-heptane. (a). Ir/TiO_2 LT catalysts; (b). Fe –Ir (1-1) / TiO_2 LT catalysts.

The catalytic activity and the total conversion of LT catalysts increases in parallel to the increases in polarity of the solvent. These result differ markedly with those obtained by Aramendía et al [25]**.** In the hydrogenation of citral in liquid phase over Pd supported catalysts. They used as supports a mixed 80:20 $SiO_2/AlPO_4$ system or a Spanish sepiolite. They found that solvents with lower dielectric constant (ε) values lead to higher reduction rates. However, Aramendía et al [30] have claimed in other contribution, that the exact effect of the solvent on the reduction of citral is rather complex and requires further investigation. It is well known that the reaction rate in a given solvent depends on the differences in the characteristics of the solvent and reactant and the solvent and the activated complex. If the activated complex is similar to the solvent but the reactant are not, the rate will be to the rate in an ideal solution in which no interactions between the reactant and solvent take place. If the reactant resemble the solvent but the transition state does not, the rate will be small compared to the ideal situation. Briefly, reactions producing products more polar than reactants will go well in polar solvent; reactions giving product less polar than the reactants will go well in non polar solvents. Thus, taking into account that during the reaction the citral molecule is adsorbed on the active center partially polarized in the carbonyl bond it should be expected that this adsorbed activated specie should reacts easier in the presence of polar solvent, in agreement with our obtained results. It can be seen in Table 3 that Ir-Fe/TiO_2 LT catalyst displays much higher activity than it monometallic counterpart. This behavior is attributed to the higher polarizability of the carbonyl bond induced by

the acidity of the catalyst. In this sample, this is an important effect, which may lead to an almost negligible effect of the dielectric constant of the solvent.

Table 3. Catalytic activity in the citral hydrogenation at 363 K and 8.27 bar, conversion level at 1h, initial activity, TOF at 10% of conversion over Ir supported catalysts. Series LT.

Catalyst	Solvent	Conversion % (t = 1h)	Initial activity μmole g^{-1} s^{-1}	TOF s^{-1}
Ir/Tio_2	n- heptane	3.0	0.12	0.010
	n-heptane-1-propanol	9.5	0.35	0.027
	1-propanol	10.2	0.37	0.028
$Ir\text{-}Fe/TiO_2$	n- heptane	19.2	0.76	0.29
	n-heptane-1-propanol	21.0	0.0.78	0.30
	1-propanol	22.5	0.88	0.34

With regard to the HT series, Figure 4 show the evolution of the conversion level with time over Ir e Ir –Fe/TiO_2 HT catalysts during the catalytic hydrogenation of citral at 363 K and 8.27 bar, for the different solvents. The observed trends are similar to those previously discussed, being higher the reaction rates at the beginning of the reaction and progressively decrease with the time on stream. The Ir/TiO_2 HT catalyst exhibits higher activity compared to the LT counterpart, which is attributed to the presence of modified metallic sites by decoration with TiO_x species. Conversely, the $Ir\text{-}Fe/TiO_2$ HT catalyst shows lower activity than the LT counterpart. This behavior is not unusual and it has been previously reported. It is attributed to the migration of TiO_x species on the $Ir\text{-}Fe^{3+}$ which produces a decrease in the activity due to a decreases in the amount of Ir surface atoms and a drop in the polarization sites. Table 4 compiles the catalytic activity results obtained in the citral hydrogenation over Ir/TiO_2 HT and $Ir\text{-}Fe/TiO_2$ HT catalysts. The values of conversion level at the same reaction time (1h), the initial activity, the turnover frequency, TOF, the selectivity and the yield to geraniol + nerol are given. As it was mentioned the catalytic activity- conversion level and the initial activity- of the Ir/TiO_2 HT catalyst is higher that the LT monometallic catalysts in the three studied solvents and increases with the polarity of the solvent, behavior explained on the basis of the modification of the active sites induced by the SMSI effect. The enhancement in the TOF values are even more important due to a decreases in the amount of Ir surface atoms. However, this catalyst displays lower selectivity to the products generated by hydrogenation of the C=O bond because by a parallel pathway the formation of acetals by reaction between the reactant and the polar solvent takes place. The formation of acetals increases with the dielectric constant of the solvent. With regard to $Ir\text{-}Fe/TiO_2$ HT catalyst the conversion level is lower compared to the LT counterpart and to the monometallic Ir/TiO_2 catalyst whatever the solvent used. This behavior is explained on the basis of destruction of surface interface sites produced by the migration of TiO_x species on $Ir\text{-}Fe^{3+}$ sites leading to a decrease in the amount of Ir surface atoms and a drop in the polarization sites.

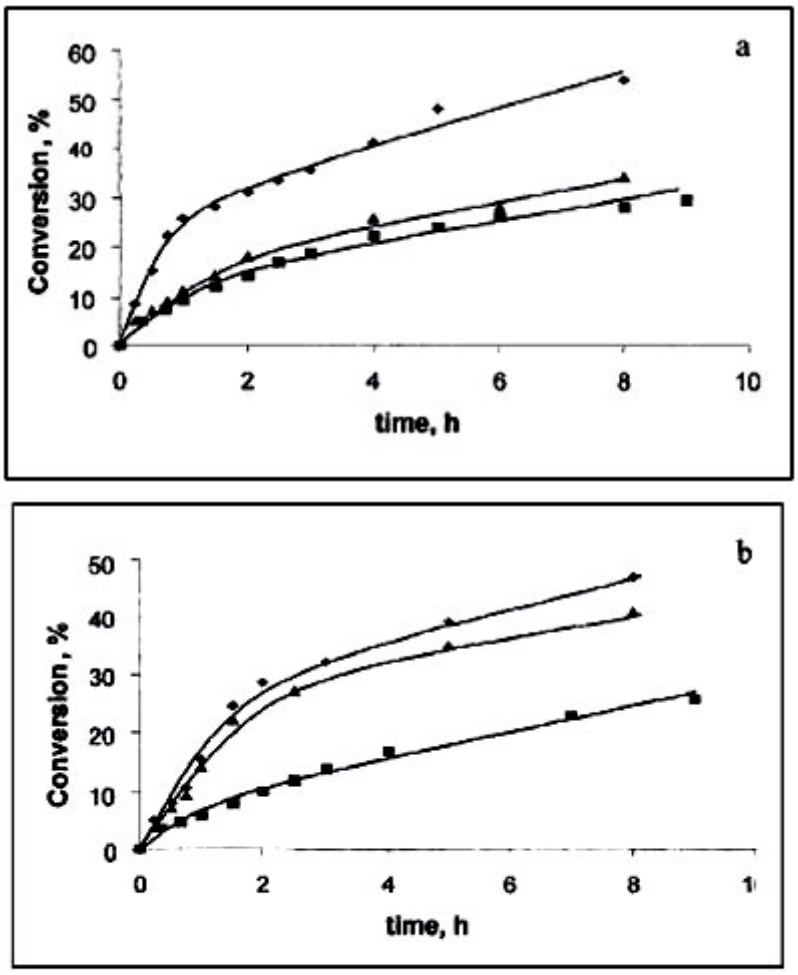

Figure 4. Evolution of the conversion level with time at 363 K and 8,27 bar in citral hydrogenation over Ir e Ir – Fe / TiO_2 HT catalysts and studied in three different solvents: (♦), 1- propanol; (▲), n- heptane y 1- propanol; (■), n- heptane (a). Ir/TiO_2 catalysts; (b). Fe –Ir (1-1) / TiO_2 catalysts

Table 4. Catalytic activity in the citral hydrogenation at 363 K and 8.27 barconversion level at 1h, initial activity , TOF and selectivity at 10% of conversion over Ir supported catalysts. Series HT.

Catalyst	Solvent	Conversión % (t=1h)	Initial activity μmole $s^{-1}g^{-1}$	TOF s^{-1}	Selectivity %	
					Geraniol + Nerol	Acetals
Ir/TiO_2	n-heptane	9	0.31	0.04	100	0
	n-heptane-1-propanol	11	0.41	0.05	95	5
$Ir-Fe/TiO_2$	1-propanol	25.5	1.19	0.14	75	25
	n-heptane	5.9	0.18	0.18	100	0
	n-heptane-1-propanol	14	0.46	0.45	70	30
	1-propanol	15.2	0.52	0.51	55	45

Additionally, the production of acetals increases significantly as the dielectric constant of the solvent increases. It has been reported by Ando et al [34] for Co/Al_2O_3 catalys that during the hydrogenation of unsaturated aldehydes, acetals can be formed if the solvent is an alcohol (ethanol). Figure 5 displays a possible route to produce acetals over acid sites in line with Capelletti et al [35] suggestions. It is a similar mechanism to that proposed for the reaction in homogeneous phase to obtain acetals from aldehydes. Thus, the protonation of the oxygen atom in the carbonyl bond takes place in the initial step. This protonation is caused by an acid site from the catalytic surface followed by a subsequent nucleophilic attack of an alcohol molecule and then lost of proton from the generated specie (protonated hemiacetal) to produce water. Finally, the acetal is obtained between a second alcohol molecule and the formed carbocation.

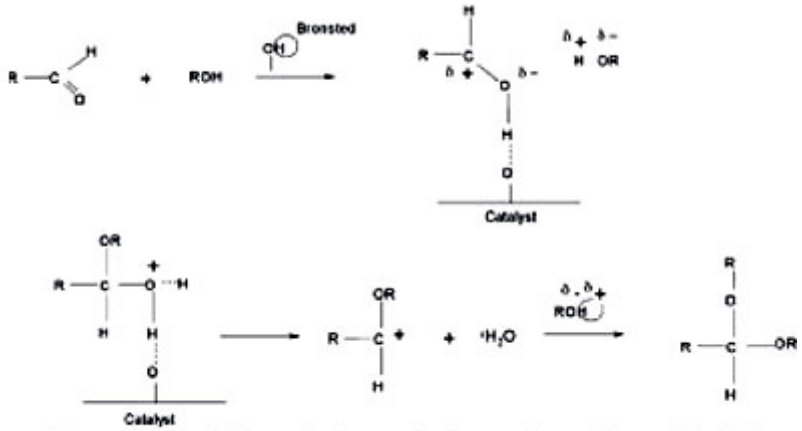

Figure 5. Possible mechanism to obtain acetals over Brönsted acid sites.

CONCLUSIONS

The obtained results showed that Ir/TiO_2 catalysts are active and selective to get geraniol and nerol by hydrogenation of citral. The system is sensitive to the reduction temperature. Increasing the reduction temperature from 473 to 773 K, LT and HT respectively lead to an important enhancement due to decoration of Ir crystals by SMSI effect. In the Ir/TiO_2 LT, the addition of Fe increases significantly the activity due to the modification of the active sites by creation of more polarizing sites. However, the $Ir\text{-}Fe/TiO_2$ HT catalyst displays lower activity because of the destruction of these polarizing sites by migration of TiO_x species.

The effect of the nature of the solvent was also studied. The results demonstrated that in the LT series, the activity increases as the dielectrical constant of the solvent increases. In these catalysts, only geraniol and nerol, the products generated by hydrogenation of the carbonyl bond, takes place. In the HT series, it was found that as the polarity of the solvent increases, a side reaction occurring on the acid sites of the catalysts lead to acetals, therefore the selectivity to the unsaturated alcohols decreases.

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